

## 0869-7021(199609)14:3&lt;251::AID-JCCE251&gt;3.0.CO;2-L

1. An integrated process for the production of a dialkyl carbonate and a diol from an alkylene oxide, carbon dioxide and an aliphatic monohydric alcohol comprising:

15 (b) reacting said cyclic carbonate with an aliphatic monohydric alcohol in the presence of said homogeneous carbonation catalyst to provide a crude product stream comprising a dialkyl carbonate and diol.

$$\begin{array}{c} \text{R}_1 - \text{R}_2 \\ \diagdown \quad \diagup \\ \text{O} \end{array}$$

said aliphatic monohydric alcohol is of the formula:

EL063715091US

wherein  $R_3$  is a monovalent aliphatic  $C_1$ - $C_{12}$  hydrocarbon group which is unsubstituted or substituted with at least one substituent selected from the group consisting of a  $C_1$ - $C_{10}$  alkyl group and a  $C_6$ - $C_{10}$  aryl group.

5        3.        The process of Claim 1, wherein said homogeneous carbonation catalyst comprises a basic component and a halide containing component.

10        4.        The process of Claim 3, wherein said basic component is selected from the group consisting of: carbonates, bicarbonates, acetates, amines, phosphines and mixtures thereof, and said halide containing component is selected from the group consisting of: alkali halides, quaternary ammonium halides and mixtures thereof.

15        5.        The process of Claim 1, wherein said pressure is in the range of about 3448 kPa to 6897 kPa (500 to 1000 psig) and the temperature is in the range of about 150 to 200°C.

20        6.        The process of Claim 1, wherein the molar ratio of  $CO_2$  to alkylene oxide is in the range from about 1.05 to 1.10 and the molar ratio of aliphatic monohydric alcohol to cyclic carbonate is in the range from about 2:1 to 6:1.

25        7.        The process of Claim 1, wherein said crude cyclic carbonate stream further comprises glycol impurities in an amount of up to 40% by weight, based upon total weight of said crude cyclic carbonate stream.

30        8.        The process of Claim 7, wherein said cyclic carbonate is ethylene carbonate, said aliphatic monohydric alcohol is methanol, and said glycol impurities comprise ethylene glycol and higher molecular weight glycols.

35        9.        The process of Claim 1, wherein said aliphatic monohydric alcohol contains dialkyl carbonate in an amount of up to 40% by weight, based upon the total weight of said aliphatic monohydric alcohol and said dialkyl carbonate.

40        10.       The process of Claim 1, further comprising a step of recovering said dialkyl carbonate and said diol from said crude product stream.

11. The process of Claim 1, further comprising:

- 5 (i) separating a first recycle stream comprising unreacted aliphatic monohydric alcohol from said crude product stream;
- (ii) recycling said first recycle stream to transesterification step (b);
- (iii) separating a second recycle stream comprising unreacted cyclic carbonate and said homogeneous carbonation catalyst from said crude product stream; and
- 10 (iv) recycling at least a portion of said second recycle stream to said carbonation step (a) and/or at least a portion of said second recycle stream to said transesterification step (b).

12. The process of Claim 2, wherein said cyclic carbonate is ethylene carbonate and said aliphatic monohydric alcohol is methanol.

13. The process of Claim 1, wherein said transesterification step (b) occurs in a reaction vessel selected from the group consisting of: a reactive distillation column, a distillation column with at least a plurality of reaction zones, a distillation column with a plurality of reaction zones having heat exchangers disposed between the distillation column and each reaction zone, and a distillation column with a plurality of reaction zones wherein bottoms thereof are optionally recycled to the distillation column.

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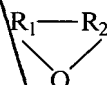
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14. An integrated process for the production of a dialkyl carbonate and a diol from an alkylene oxide, carbon dioxide and an aliphatic monohydric alcohol comprising:

- 25 (a) reacting an alkylene oxide with carbon dioxide in the presence of a homogeneous carbonation catalyst to provide a crude cyclic carbonate stream comprising a cyclic carbonate and said homogeneous catalyst; and

(b) reacting said cyclic carbonate and said homogeneous carbonation catalyst with an aliphatic monohydric alcohol in the presence of a heterogeneous transesterification catalyst to provide a crude product stream comprising a dialkyl carbonate and diol.

15. The process of Claim 14, wherein said alkylene oxide is of the formula:



wherein  $\text{R}_1$  and  $\text{R}_2$  independently of one another denote a divalent group represented by the formula  $-(\text{CH}_2)_m-$ , wherein  $m$  is an integer from 1 to 3, which is unsubstituted or substituted with at least one substituent selected from the group consisting of a  $\text{C}_1$ - $\text{C}_{10}$  alkyl group and a  $\text{C}_6$ - $\text{C}_{10}$  aryl group, wherein  $\text{R}_1$  and  $\text{R}_2$  can share the same substituent; and

said aliphatic monohydric alcohol is of the formula:



wherein  $\text{R}_3$  is a monovalent aliphatic  $\text{C}_1$ - $\text{C}_{12}$  hydrocarbon group which is unsubstituted or substituted with at least one substituent selected from the group consisting of a  $\text{C}_1$ - $\text{C}_{10}$  alkyl group and a  $\text{C}_6$ - $\text{C}_{10}$  aryl group.

16. The process of Claim 14, wherein said homogeneous carbonation catalyst is at least one catalyst selected from the group consisting of: alkali metal halides, ammonium halides, quaternary ammonium halides, phosphonium halides, arsonium halides and mixtures thereof.

17. The process of Claim 16, wherein said homogeneous carbonation catalyst is tetraethyl ammonium bromide or potassium iodide.

18. The process of Claim 14, wherein said heterogeneous transesterification catalyst is at least one catalyst selected from the group

consisting of: anion exchange resins, inorganic metal oxides and inorganic solid support catalysts containing metals, and compounds or complexes of at least one element of groups 1, 2, 4-10, 12, or 13-17 of the periodic table.

5           19.       The process of Claim 14, wherein said heterogeneous transesterification catalyst comprises a transitional alumina.

10           20.       The process of Claim 14, wherein said crude cyclic carbonate stream further comprises glycol impurities in an amount of from about 0.5 to 40% by weight, based upon the total weight of said crude cyclic carbonate stream.

15           21.       The process of Claim 20, wherein said cyclic carbonate is ethylene carbonate, said aliphatic monohydric alcohol is methanol, and said glycol impurities comprise ethylene glycol and higher molecular weight glycols.

20           22.       The process of Claim 14, wherein said aliphatic monohydric alcohol further comprises dialkyl carbonate in an amount of up to 15% by weight, based upon the total weight of said aliphatic monohydric alcohol and said dialkyl carbonate.

25           23.       The process of Claim 14, further comprising the step of recovering said dialkyl carbonate and said diol from said crude product stream.

30           24.       The process of Claim 14, further comprising:  
          (i) separating a first recycle stream comprising unreacted aliphatic monohydric alcohol from said crude product stream;  
          (ii) recycling said first recycle stream to transesterification step (b);  
          (iii) separating a second recycle stream comprising unreacted cyclic carbonate and said homogeneous carbonation catalyst from said crude product stream; and

(iv) recycling at least a portion of said second recycle stream to carbonation step (a) and at least a portion of said second recycle stream to said transesterification step (b).

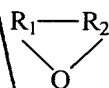
5           25.     The process of Claim 15, wherein said cyclic carbonate is ethylene carbonate and said aliphatic monohydric alcohol is methanol.

10           26.     The process of Claim 14, wherein said transesterification step (b) occurs in a reaction vessel selected from the group consisting of: a reactive distillation column, a distillation column with at least a plurality of reaction zones, a distillation column with a plurality of reaction zones having heat exchangers disposed between the distillation column and each reaction zone, and a distillation column with a plurality of reaction zones wherein bottoms thereof are optionally recycled to the distillation column.

15           27.     An integrated process for the production of a dialkyl carbonate and a diol from an alkylene which comprises:

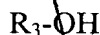
- (a) reacting said alkylene with an oxygen-containing gas, thereby producing an alkylene oxide, carbon dioxide, and water;
- 20           (b) reacting at least portion of said alkylene oxide with said carbon dioxide in the presence of a homogeneous carbonation catalyst at a temperature in the range of about 50 to 250°C and at a pressure of at least about 1379 kPa (200 psig) to provide a crude cyclic carbonate stream comprising a cyclic carbonate and homogeneous carbonation catalyst; and
- 25           (c) reacting said cyclic carbonate with an aliphatic monohydric alcohol in the presence of said homogeneous carbonation catalyst to provide a crude product stream comprising a dialkyl carbonate and diol.

28. The process of claim 27, wherein said alkylene oxide is of the formula:



wherein  $R_1$  and  $R_2$  independently of one another denote a divalent group represented by the formula  $-(CH_2)_m-$ , wherein  $m$  is an integer from 1 to 3, which is unsubstituted or substituted with at least one substituent selected from the group consisting of  $C_1$ - $C_{10}$  alkyl group and a  $C_6$ - $C_{10}$  aryl group, wherein  $R_1$  and  $R_2$  can share the same substituent; and

said aliphatic monohydric alcohol is of the formula:



wherein  $R_3$  is a monovalent aliphatic  $C_1$ - $C_{12}$  hydrocarbon group which is unsubstituted or substituted with at least one substituent selected from the group consisting of a  $C_1$ - $C_{10}$  alkyl group and a  $C_6$ - $C_{10}$  aryl group.

29. The process of Claim 27, wherein said homogeneous carbonation catalyst comprises a basic component and a halide containing component.

30. The process of Claim 29, wherein said basic component is selected from the group consisting of carbonates, bicarbonates, acetates, amines, phosphines and mixtures thereof and said halide containing component is selected from the group consisting of alkali halides, quaternary ammonium halides and mixtures thereof.

31. The process of Claim 27, wherein said pressure is in the range of about 3448 kPa to 6897 kPa (500 to 1000 psig) and the temperature is in the range of about 150 to 200°C.

32. The process of Claim 27, wherein the molar ratio of  $CO_2$  to alkylene oxide is in the range from about 1.05 to 1.10 and the molar ratio of

aliphatic monohydric alcohol to cyclic carbonate is in the range from about 2:1 to 6:1.

5 33. The process of Claim 27, wherein said crude cyclic carbonate stream further comprises glycol impurities in an amount of up to 40% by weight, based upon total weight of said crude cyclic carbonate stream.

34. The process of Claim 33, wherein said cyclic carbonate is ethylene carbonate, said aliphatic monohydric alcohol is methanol, and said glycol impurities comprise ethylene glycol and higher molecular weight glycols.

10 35. The process of Claim 27, wherein said aliphatic monohydric alcohol contains dialkyl carbonate in an amount of up to 40% by weight, based upon the total weight of said aliphatic monohydric alcohol and said concomitant dialkyl carbonate.

36. The process of Claim 27, further comprising the further step of recovering said dialkyl carbonate and said diol from said crude product stream.

15 37. The process of Claim 27, further comprising:

- (i) separating a first recycle stream comprising unreacted aliphatic monohydric alcohol from said crude product stream;
- (ii) recycling said first recycle stream to the transesterification step (c);
- 20 (iii) separating a second recycle stream comprising unreacted cyclic carbonate and said homogeneous carbonation catalyst from said crude product stream; and
- (iv) recycling at least a portion of said second recycle stream to carbonation step (b) and/or at least a portion of said second recycle stream to said  
25 transesterification step (c).



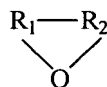
38. The process of Claim 28, wherein said alkylene is ethylene, said cyclic carbonate is ethylene carbonate and said aliphatic monohydric alcohol is methanol.

39. The process of Claim 27, wherein the transesterification step (c) occurs in a reaction vessel selected from the group consisting of: a reactive distillation column, a distillation column with at least a plurality of reactors, a distillation column with a plurality of reactors having heat exchangers disposed between the distillation column and each reactor, and a distillation column with a plurality of reactors wherein bottoms thereof are optionally recycled to the distillation column.

40. An integrated process for the production of a dialkyl carbonate and a diol from an alkylene which comprises:

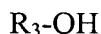
- (a) reacting at least a portion of said alkylene with an oxygen-containing gas, thereby producing an alkylene oxide, carbon dioxide, and water;
- (b) reacting at least a portion of said alkylene oxide with said carbon dioxide in the presence of a homogeneous carbonation catalyst at a temperature in the range of about 50 to 250°C and at a pressure of at least about 1379 kPa (200 psig) to provide a crude cyclic carbonate stream comprising a cyclic carbonate and said homogeneous catalyst; and
- (c) reacting said cyclic carbonate and said homogeneous carbonation catalyst with an aliphatic monohydric alcohol in the presence of heterogeneous transesterification catalyst to provide a crude product stream comprising a dialkyl carbonate and diol.

41. The process of Claim 40, wherein said alkylene oxide is of the formula:



wherein  $R_1$  and  $R_2$  independently of one another denote a divalent group represented by the formula  $-(CH_2)_m-$ , wherein  $m$  is an integer from 1 to 3, which is unsubstituted or substituted with at least one substituent selected from the group consisting of a  $C_1$ - $C_{10}$  alkyl group and a  $C_6$ - $C_{10}$  aryl group, wherein  $R_1$  and  $R_2$  can share the same substituent; and

said aliphatic monohydric alcohol is of the formula:



wherein  $R_3$  is a monovalent aliphatic  $C_1$ - $C_{12}$  hydrocarbon group which is unsubstituted or substituted with at least one substituent selected from the group consisting of a  $C_1$ - $C_{10}$  alkyl group and a  $C_6$ - $C_{10}$  aryl group.

42. The process of Claim 40, wherein said homogeneous carbonation catalyst is at least one catalyst selected from the group consisting of: alkali metal halides, ammonium halides, quaternary ammonium halides, phosphonium halides, arsonium halides and mixtures thereof.

43. The process of Claim 42, wherein said homogeneous carbonation catalyst is tetraethyl ammonium bromide or potassium iodide.

44. The process of Claim 40, wherein said heterogeneous transesterification catalyst is at least one catalyst selected from the group consisting of: anion exchange resins, inorganic metal oxides and inorganic solid support catalysts containing metals, and compounds or complexes of at least one element of groups 1, 2, 4-10, 12, or 13-17 of the periodic table.

45. The process of Claim 40, wherein said heterogeneous transesterification catalyst comprises a transitional alumina.

46. The process of Claim 40, wherein said crude cyclic carbonate stream further comprises glycol impurities in an amount of from about 0.5 to 40% by weight, based upon the total weight of said crude cyclic carbonate stream.

5 47. The process of Claim 46, wherein said cyclic carbonate is ethylene carbonate, said aliphatic monohydric alcohol is methanol, and said glycol impurities comprise ethylene glycol and higher molecular weight glycols.

10 48. The process of Claim 40, wherein said aliphatic monohydric alcohol further comprises dialkyl carbonate in an amount of up to 15% by weight, based upon the total weight of said aliphatic monohydric alcohol and said dialkyl carbonate.

15 49. The process of Claim 40, further comprising the step of recovering said dialkyl carbonate and said diol from said crude product stream.

50. The process of Claim 40, further comprising:

- 20 (i) separating a first recycle stream comprising unreacted aliphatic monohydric alcohol from said crude product stream;
- (ii) recycling said first recycle stream to the transesterification step (c);
- (iii) separating a second recycle stream comprising unreacted cyclic carbonate and said homogeneous carbonation catalyst from said crude product stream; and
- 25 (iv) recycling at least a portion of said second recycle stream to the carbonation step (b) and at least a portion of said second recycle stream to said transesterification step (c).

30 51. The process of Claim 41, wherein said cyclic carbonate is ethylene carbonate and said aliphatic monohydric alcohol is methanol.

52. The process of Claim 40, wherein said transesterification step (c) occurs in a reaction vessel selected from the group consisting of: a reactive distillation column, a distillation column with at least a plurality of reactors, a distillation column with a plurality of reactors having heat exchangers disposed  
5 between the distillation column and each reactor, and a distillation column with a plurality of reactors wherein bottoms thereof are optionally recycled to the distillation column.

53. A process for producing polycarbonate which comprises the following steps:

- 10 (a) reacting an alkylene with an oxygen-containing gas, thereby producing an alkylene oxide, carbon dioxide, and water;
- 15 (b) reacting at least a portion of said alkylene oxide with said carbon dioxide in the presence of a homogeneous carbonation catalyst at a temperature in the range of about 50 to 250°C and at a pressure of at least about 1379 kPa (200 psig) to provide a crude cyclic carbonate stream comprising a cyclic carbonate and homogeneous catalyst;
- 20 (c) reacting said cyclic carbonate with an aliphatic monohydric alcohol in the presence of said homogeneous transesterification catalyst to provide a crude product stream comprising a dialkyl carbonate and diol;
- 25 (d) separating said dialkyl carbonate from said diol, thereby producing a dialkyl carbonate-enriched stream;
- (e) reacting said dialkyl carbonate-enriched stream and phenol in the presence of a metal-containing catalyst at a temperature in the range between about 80 to 300°C and at a pressure in the range between about 2 kPa to 4000 kPa (absolute pressure), thereby producing diphenyl carbonate and alkanol;

- (f) separating said diphenyl carbonate from said alkanol, thereby producing a diphenyl carbonate-enriched stream;
- (g) reacting said diphenyl carbonate-enriched stream with bisphenol-A, thereby producing polycarbonate and phenol; and
- 5 (h) separating said polycarbonate from said phenol, thereby producing a polycarbonate-enriched stream.

54. A process for producing polycarbonate which comprises the following steps:

- 10 (a) reacting an alkylene with an oxygen-containing gas, thereby producing an alkylene oxide, carbon dioxide, and water;
- (b) reacting at least a portion of said alkylene oxide with said carbon dioxide in the presence of a homogeneous carbonation catalyst at a temperature in the range of about 50 to 250°C and at a pressure of at least about 1379 kPa (200 psig) to provide a crude cyclic carbonate stream comprising a cyclic carbonate and homogeneous carbonate catalyst;
- 15 (c) reacting said cyclic carbonate and said homogeneous carbonation catalyst with an aliphatic monohydric alcohol in the presence of said heterogeneous transesterification catalyst to provide a crude product stream comprising a dialkyl carbonate and diol;
- 20 (d) separating said dialkyl carbonate from said diol, thereby producing a dialkyl carbonate-enriched stream;
- 25 (e) reacting said dialkyl carbonate-enriched stream and phenol in the presence of a metal-containing catalyst at a temperature in the range between about 80 to 300°C and at a pressure in the

range between about 2 kPa to 4000 kPa (absolute pressure, thereby producing diphenyl carbonate and alkanol;

- (f) separating said diphenyl carbonate from said alkanol, thereby producing a diphenyl carbonate-enriched stream;
- (g) reacting said diphenyl carbonate-enriched stream with bisphenol-A, thereby producing polycarbonate and phenol; and
- (h) separating said polycarbonate from said phenol, thereby producing a polycarbonate-enriched stream.

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